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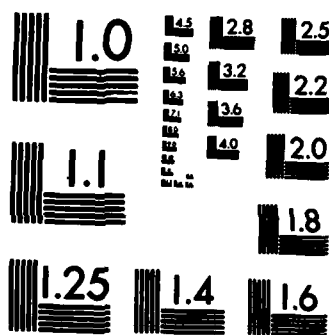
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C. Neuberger, C. C. (Paul) Hsu and
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MgSO₄ solutions with the addition of up to 0.12 molar NaCl, the theory is in good agreement with the data of Hsu and Fisher and in substantial conflict with the data in 0.017 molar MgSO₄ mixtures with NaCl of Kurtze and Tamm. For 0.1 and 0.17 molar MgSO₄ solutions, the data of Kurtze and Tamm are in better agreement with theory. The extension to high ionic strength of Debye-Huckel theory derived for low ionic strength is discussed briefly.

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EFFECT OF IONIC STRENGTH AND ION PAIRING ON SOUND ABSORPTION IN AQUEOUS SOLUTIONS OF MgSO_4 AND NaCl

C. Neuberger, C. C. Hsu and F. H. Fisher

ABSTRACT

Sound absorption in aqueous solutions of MgSO_4 is reduced by the addition of NaCl . From the Eigen and Tamm multistate dissociation theory it can be shown that the absorption exhibited by MgSO_4 is proportional to the ion-pair concentration. The reduction in sound absorption observed upon the addition of NaCl is treated theoretically and is attributed to two effects; formation of NaSO_4^- and MgCl^+ ion-pairs and an increase in ionic strength, both of which reduce the concentration of MgSO_4 ion pairs. Comparisons between theory and experiment support the theoretical treatment presented. For 0.02 molar MgSO_4 solutions with the addition of up to 0.12 molar NaCl , the theory is in good agreement with the data of Hsu and Fisher and in substantial conflict with the data in 0.017 molar MgSO_4 mixtures with NaCl of Kurtze and Tamm. For 0.1 and 0.17 molar MgSO_4 solutions, the data of Kurtze and Tamm are in better agreement with theory. The extension to high ionic strength of Debye-Huckel theory derived for low ionic strength is discussed briefly.

INTRODUCTION

Below 300 kHz sound absorption in low concentration aqueous MgSO_4 solutions exceeds that due to pure water; for example, in a 0.02 molar solution at 25° the absorption due to a pressure dependent chemical relaxation exceeds the water value by a factor of 37 [1] at frequencies well below the 100 kHz relaxation frequency. When NaCl is added to MgSO_4 solutions, the absorption due to MgSO_4 is reduced substantially as Kurtze and Tamm [2] first demonstrated; for a ratio $[\text{NaCl}]/[\text{MgSO}_4] = 5$, their results indicated a reduction of half in absorption, independent of the initial MgSO_4 concentration of 0.017, 0.1 and 0.17 moles/liter.

Kurtze and Tamm attributed the decrease in absorption to the reduction of MgSO_4 ion-pairs due to the formation of MgCl^+ and NaSO_4^- ion-pairs. That the sound absorption in the mixture is due to MgSO_4 ion-pairs was shown both by Kurtze and Tamm and Wilson and Leonard [3] [4] since neither MgCl_2 , Na_2SO_4 nor NaCl solution exhibit significant absorption below 300 kHz. These results have been discussed in the extensive review by Stuehr and Yeager [5] of acoustic research in electrolyte solutions. Recent work by Hsu and Fisher [6] found that a 0.03 M Na_2SO_4 solution would exhibit the same absorption as that by pure water in the frequency range of 30-300 kHz. These results for Na_2SO_4 are in agreement with data extrapolated from results obtained at higher frequencies and concentrations by Gilligan and Atkinson [7] in Na_2SO_4 solutions.

Eigen, Kurtze and Tamm [8] attempted to account quantitatively for the observed reduction based on NaSO_4^- ion-pairing; however, they used the same dissociation constant for NaSO_4^- and MgSO_4 . Bies [9] attempted to account for the reduction on the basis of ionic strength effects on activity coefficients. In analyzing conductance data, Fisher [10] and Fisher and Fox [11] used the Kurtze and Tamm results in arguing for greater association in Na_2SO_4 solutions, that is, a decrease in the dissociation constant of 0.19 reported by Jenkins and Monk [12] to a value of 0.10. Fisher and Fox [11] also reported dissociation constants for MgCl^+ ion pairing.

The purpose of this paper is to account for the reduction of sound absorption in MgSO_4 - NaCl mixtures on a theoretical basis, using the conductance results of Fisher and Fox [3] for MgCl^+ and NaSO_4^- ion pairing and the conductance results of Fisher and Fox [14] for MgSO_4 which are in close agreement with those of Pethybridge and Taba [15]. In this paper we make use of the same Debye-

Huckel (DH) equation for the activity coefficient as used in analyzing the conductance data [11] [16] [17]. We also apply the DH equation to higher ionic strength regions based on the fact that stoichiometric activity coefficients $\gamma_{\pm} = \alpha f_{\pm}$ calculated for MgSO_4 solutions up to 1 molar very closely match the experimentally derived vapor pressure and freezing point values reported by Robinson and Jones [18], as well as the values derived from the equation by Lietzke and Stoughton [19].

From our analysis we find, contrary to the experimental results of Kurtze and Tamm, that the reduction in absorption does depend on the initial MgSO_4 concentration. While our theoretical results are in fair agreement with their high concentration results, we differ greatly with their results at low concentration. We suspect that their low concentration data, the most difficult region in which to make accurate measurements, contained substantial experimental errors. Recent acoustic results reported by Hsu and Fisher [1] for the addition of NaCl to 0.02 molar MgSO_4 solutions are in good agreement with the theoretical results presented in this paper.

2. THEORY

Liebermann [20] was the first to show how sound absorption due to a pressure dependent chemical relaxation was related to the speciation and kinetics of the reaction. The absorption is expressed as follows:

$$\alpha (\text{cm}^{-1}) = \frac{\pi \beta_{ch}}{\beta_o C} \frac{f_r f^2}{f^2 + f_r^2} \quad (1)$$

where β_{ch} is the chemical compressibility (cm^2/dyne), β_o the isothermal compressibility (cm^2/dyne), C the sound velocity (cm/sec), f_r the relaxation frequency and f the acoustic frequency, both in Hz. For analysis of acoustic data in systems which demonstrate relaxation processes it is more convenient to analyze data and summarize results using the equation for absorption per wavelength:

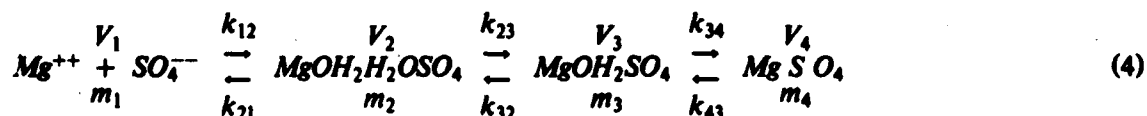
$$\alpha \lambda = \frac{\pi \beta_{ch}}{\beta_o} \frac{f_r f}{f^2 + f_r^2} \quad (2)$$

as discussed by Stuehr and Yeager, for example, or $Q\lambda$ used by Kurtze and Tamm where Q is absorption per molecule of solute:

$$Q\lambda = \frac{2\alpha\lambda}{cN^0} \quad (3)$$

where c is concentration in moles/liter and N^0 is the Avogadro constant.

Eigen and Tamm, in their extensive theoretical work to explain the absorption data of Kurtze and Tamm in MgSO_4 solutions over wide concentration (.02 to 0.2 mole/liter) and frequency ranges ($10^4 - 10^8$ Hz) postulated a multistate dissociation theory in which three species of ion pairs are involved as seen in Eq. 4:



where the V_i are the partial volumes (cc/mole) and the m_i are the concentrations in (moles/cc).

In the Eigen-Tamm normal-mode theory to explain the 100 kHz (primary relaxation per Stuehr and Yeager) and the 200-400 MHz relaxations, the chemical compressibility (β_{III}) associated with the primary relaxation is shown below (using their notation).

$$\beta_{III} = \frac{(m_1' + m_2 + m_3)m_4}{m_1' + m_2 + m_3 + m_4} \frac{(\Delta V_{III})^2}{RT}, \quad (5)$$

where m_1' is a concentration term including consideration of activity coefficients and ΔV_{III} is a

normalized volume change consisting of a linear combination of the $(V_i - V_{i+1})$ as in Eq. 4. From Eq. 5 it is seen that if m_4 is a small fraction of the total ion pair concentration, $m_4 \ll m_2 + m_3 + m_4$, the chemical compressibility and therefore the absorption can be written as:

$$\beta_{III} = \frac{m_4 (\Delta V_{III})^2}{RT} \quad (6)$$

$$\text{and } \alpha\lambda = \frac{\pi m_4 (\Delta V_{III})^2}{\beta^0 RT} \frac{ff_r}{f^2 + f_r^2} \quad (7)$$

Since m_4 is directly proportional to the total ion-pair concentration, we see that sound absorption is therefore directly proportional to the total ion-pair concentration for a constant ΔV_{III} and negligible changes in β_0 .

The assumption that m_4 is a small fraction of all the ion pairs is supported by measurements of the effect of pressure on conductance and absorption in MgSO_4 solutions [21] [22]. Briefly, for a change of 1000 atm, the ion-pair concentration decreases only by 10% whereas the absorption drops by a factor of three. This paradoxical behavior as discussed by Fisher and Fox [14], is consistent with the multistate dissociation model though exact agreement has yet to be achieved. Failure to obtain exact agreement does not diminish the multistate theory. That the agreement is as good as it is must be considered remarkable because The Eigen and Tamm multistate model, deduced to explain the ultrasonic spectrometry data of Kurtze and Tamm, was derived solely from atmospheric pressure data. Since absorption is proportional to the product of a concentration times the square of a volume change, a range of parameters for the equilibrium constants and ΔV values were used by Eigen and Tamm in their multistate model, $\pm 50\%$ for the equilibrium constants and $\pm 20\%$ for the ΔV terms. The set of values which best described both the acoustic and conductance data as a function of pressure indicated that m_4 is only about 5% of the total ion pair concentration. This is the basis for the assumption that $m_4 \ll m_2 + m_3 + m_4$, thereby justifying the use of Eqn. (7).

We proceed then on the basis that sound absorption in MgSO_4 -NaCl mixtures is a measure of ion-pairing of MgSO_4 since Na_2SO_4 , MgCl_2 and NaCl solutions exhibit negligible absorption. Consequently, as NaCl is added to an MgSO_4 solution a reduction in absorption is attributed to a decrease in ion pairing of MgSO_4 . Fisher [23] applied this concept to sound absorption in sea water, using the absorption to deduce the concentration of MgSO_4 ion-pairs in a complex mixed electrolyte solution at high ionic strength, $I = 0.7$, where the NaCl concentration is more than 10 times the concentration of the Mg or SO_4 ions. The results for seawater were in good agreement with the theoretical modelling of Garrels and Thompson [24].

If we denote the neutral ion pair concentration for MgSO_4 as $[\text{MgSO}_4^0]$ we then write:

$$\frac{(\beta_{III})_M}{(\beta_{III})_O} = \frac{(m_4)_M}{(m_4)_O} = \frac{[\text{MgSO}_4^0]_M}{[\text{MgSO}_4^0]_O} \quad (8)$$

for the mixture (M) and initial (O) pure solutions. Note that in Eq. (7) the maximum absorption per wavelength $(\alpha\lambda)_{\max}$ occurs when $f = f_r$ and that Eq. (8) can be rewritten as (assuming negligible change in β_0 or ΔV_{III})

$$\frac{(\alpha\lambda_{\max})_M}{(\alpha\lambda_{\max})_O} = \frac{[\text{MgSO}_4^0]_M}{[\text{MgSO}_4^0]_O} \quad (9)$$

3. METHOD OF CALCULATION

The calculations to evaluate the right hand side of Eqn. (9) are relatively straightforward, requiring only the dissociation constants of 0.0062 [14], 0.1 [13] and 0.178 [13] for MgSO_4 , NaSO_4^- and MgCl^+ respectively. The Debye-Huckel equation [25] [26] [27]

$$-\log f_{ij} = A|z_i z_j| \frac{\sqrt{I}}{1 + Ba_{ij}\sqrt{I}} \quad (10)$$

is used to calculate the activity coefficients in the equations:

$$K_1 = \frac{[Mg^{++}][SO_4^{--}]f_{12}^2}{[MgSO_4]}, \quad (11)$$

$$K_2 = \frac{[Na^+][SO_4^{--}]f_{12}f_{21}}{[NaSO_4]f_{11}}, \quad (12)$$

$$K_3 = \frac{[Mg^{++}][Cl^-]f_{21}f_{12}}{[MgCl^+]f_{11}}, \quad (13)$$

where the ionic strength $I = 0.5 \sum C_i z_i^2$ which, of course, includes the charged ion pairs. Values for A and B are the usual Debye-Huckel values at 25° and the a_{ij} values are 11.58, 5.79 and 2.90 Å for the 2-2, 1-2 or 2-1, and 1-1 activity coefficients. The a_{ij} value of 11.58 Å is based on the results of Fisher and Fox [14] for $MgSO_4$ and we use the Bjerrum [28] idea of making the distance proportional to the product of the charges to get the other a_{ij} values.

The procedure is to solve the above equations (10)-(13) to determine the initial and final concentration of $MgSO_4$ in Eqn. (9) for pure $MgSO_4$ and the mixtures as NaCl is added.

Since there is an increase in ionic strength, some of the reduction in $MgSO_4$ will be due to ionic strength effects on the activity coefficient and the remainder will be due to ion-pairing effects. To separate these two effects we calculate the decrease in $MgSO_4$ ion pairs due to the increased ionic strength as if no $NaSO_4^-$ and $MgCl^+$ ion pairing occurred, but at the same ionic strength calculated using Eqns. (10)-(13) and the dissociation constants given above; the ionic strength effect, therefore, is calculated at the same ionic strength including all pairing. The remainder of the decrease in $MgSO_4$ is then attributed to ion-pairing effects. This artificial separation of the two effects provides insight into their relative significance.

In this work we have used Eqn. (10) over a wide range of ionic strengths, a procedure which is certainly open to challenge. However, since our analysis is on a differential basis, errors in absolute values of concentration will offset one another, and also free activity coefficients calculated with Eqn. (10) are consistent with the stoichiometric activity coefficients of Robinson and Jones. Therefore, the work reported here should be regarded as an initial step in making a critical evaluation of the relation between acoustic data and thermodynamic dissociation constants obtained from independent data.

4. DISCUSSION OF RESULTS

The results of our calculations are shown partially in Table I and more completely in Fig. 1 in which we compare our results with the experimental data of Kurtze and Tamm. To facilitate numerical comparison of our results with those of Kurtze and Tamm we make use of the empirical formula they used to summarize their results:

$$\frac{A}{A_0} = \frac{[MgSO_4]}{[MgSO_4] + F[NaCl]}, \quad (14)$$

where A is sound absorption in the $MgSO_4$ -NaCl mixture and A_0 is absorption in pure $MgSO_4$ solution. In the context of our theoretical treatment

$$\frac{A}{A_0} = \frac{[MgSO_4]_M}{[MgSO_4]_O} = \frac{(\alpha\lambda)_M}{(\alpha\lambda)_O}. \quad (15)$$

If we rewrite Eq. (16) as follows:

$$\frac{A_0 - A}{A} = F \frac{[NaCl]}{[MgSO_4]} = FR, \quad (16)$$

we then see how Fig. 1 relates the absorption data in terms of the intercept F for equal concentrations of NaCl and MgSO_4 . The greater the reduction in absorption whether due to ion-pairing or ionic strength effects, the greater value of F . Therefore, in the MgSO_4 - NaCl system, F is a measure of ion association for NaSO_4^- and MgCl^+ as well as of ionic strength.

Whereas Kurtze and Tamm experimentally arrived at the conclusion that $F = 0.21$, a constant independent of the initial concentration of MgSO_4 our theoretical analysis indicate otherwise as seen in Fig. 1 and in Fig. 2. We may summarize our theoretical results for MgSO_4 - MgCl units shown in Fig. 2 with the equation:

$$F \approx 0.32 c^{0.27} \quad (17)$$

where c (moles/liter) is the concentration of MgSO_4 or NaCl . Fig. 3 summarizes the ionic strength and ion-pairing effects for 0.017 M MgSO_4 solutions as NaCl is added.

While our high concentration calculations agree reasonably well with the experimental data of Kurtze and Tamm as seen in Fig. 1, the low concentration (0.017 molar) results do not. However, the lower MgSO_4 concentration region is a more difficult one in which to make accurate measurements. Also, only two of the Kurtze and Tamm data points are for 0.017 M MgSO_4 . Recent work by Hsu [1] for 0.02 molar MgSO_4 aqueous solutions with values of $R = 1, 2, 4$ and 6 for the addition of NaCl yielded $F = 0.129$, in good agreement with the value of $F = 0.134$ calculated according to the theory in this paper and as shown numerically in Fig. 1. If the dissociation constants for NaSO_4^- and MgCl^+ are doubled, we see in Table II that the theoretically derived value for F is outside the range of experimental error in the work reported by Hsu and Fisher [1]. Other variations of the theoretical calculations are shown in Table II, all of which provide support for the dissociation constants we used, namely, .0062, 0.1 and 0.178 for MgSO_4 , NaSO_4^- and MgCl^+ , respectively. With further refinements it is felt that the experimental error can be reduced so that the acoustic data can provide a more accurate basis for analysis of dissociation constants.

Therefore, we have both experimental and theoretical results in fair agreement with one another at low concentrations and certainly both in disagreement with the low concentration results of Kurtze and Tamm. This initial theoretical effort to understand sound absorption in mixtures of MgSO_4 and NaCl is encouraging.

Questions arise about the use of the Debye-Huckel activity coefficient equation regarding its use in high ionic strength regions. It is therefore worthwhile to mention that stoichiometric activity coefficients for pure MgSO_4 solutions calculated with our $K = 0.0062$ are in close agreement with those reported by Robinson and Jones [18] and Lietzke and Stoughton [19] from experimental data as seen in Table III. Such agreement does not mean we are necessarily correct in our theoretical approach but only that we are not in gross disagreement with what is known. For pure MgSO_4 solutions up to 0.1 molar the absorption data of Kurtze and Tamm are proportional to the ion-pair concentration calculated using Eqs. (10) and (11).

5. CONCLUSION

In this work we have evaluated what to expect for sound absorption reduction in MgSO_4 solutions as NaCl is added, separating the effects of ionic strength and ion pairing. We find that in the empirical equation of Kurtze and Tamm, F is not independent of the concentration of MgSO_4 .

For 0.02 M MgSO_4 solutions we calculate $F = 0.134$ which is in good agreement with the value $F = 0.129$ Hsu [1] obtained with recent acoustic measurements at the same MgSO_4 concentration.

Therefore, predictions for the reduction in sound absorption as NaCl is added to MgSO_4 solutions are in good agreement with acoustic data and provides independent support for the lower dissociation constant of NaSO_4^- reported by Fisher and Fox.

The agreement with the higher concentration data of Kurtze and Tamm may be fortuitous in view of the limitations of using the Debye-Huckel activity coefficient equation as expressed in Eqn. (10) at

high ionic strengths. However, the differential basis of the calculations partially compensates for absolute errors in the concentration of MgSO_4 ion pairs. This work demonstrates in principle how sound absorption data can be used to study ion-pairing in mixed salt solutions on a quantitative basis. The agreement between the predicted and observed values of absorption in .02 M MgSO_4 -NaCl mixtures is encouraging.

ACKNOWLEDGEMENTS

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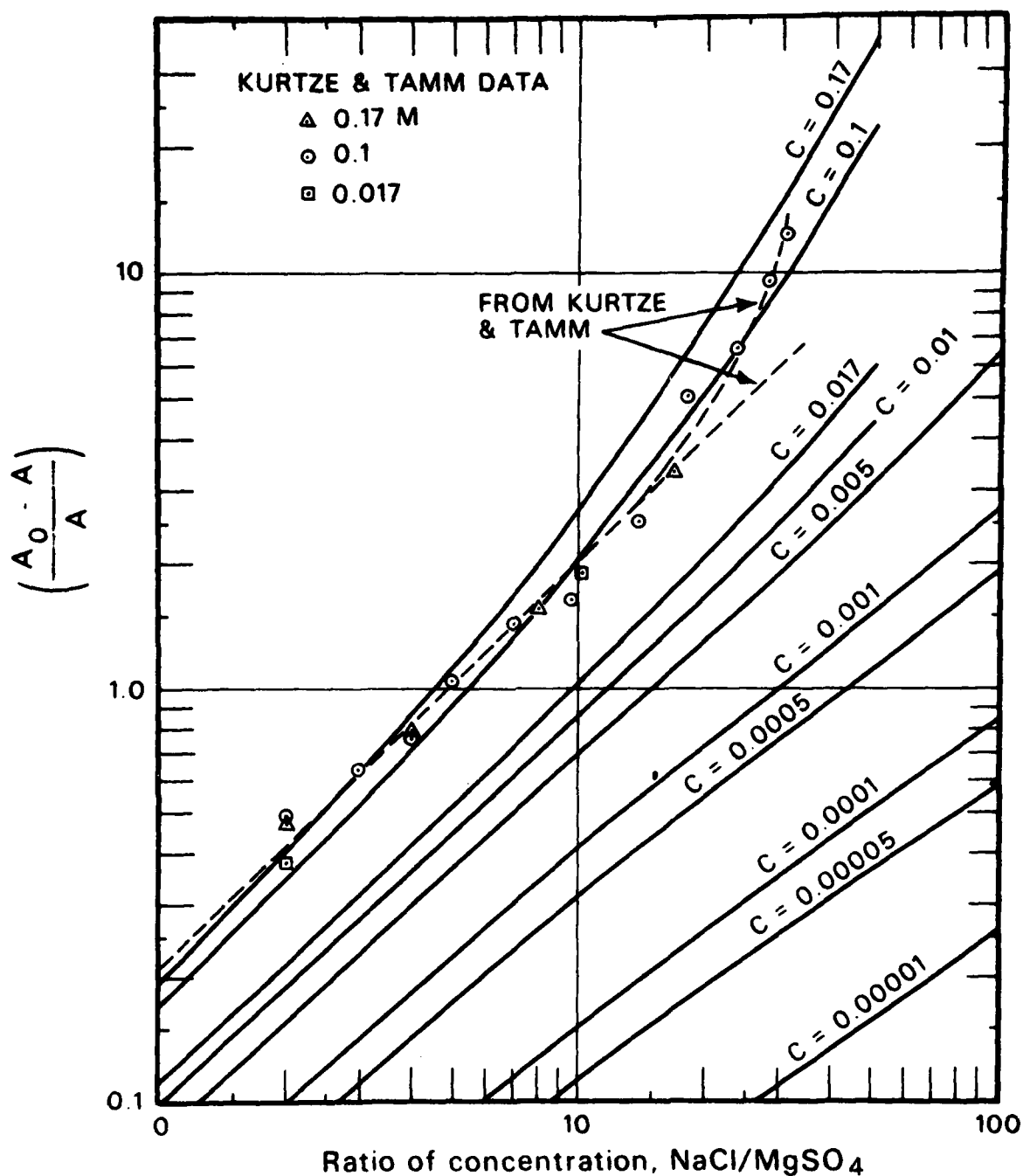


Fig. 1. Comparison of calculated and measured values of sound absorption reduction in MgSO_4 solutions as NaCl is added. Data points and dashed curves are from Kurtze and Tamm at 20°C. Solid curves are calculated values for each MgSO_4 concentration at 25°C.

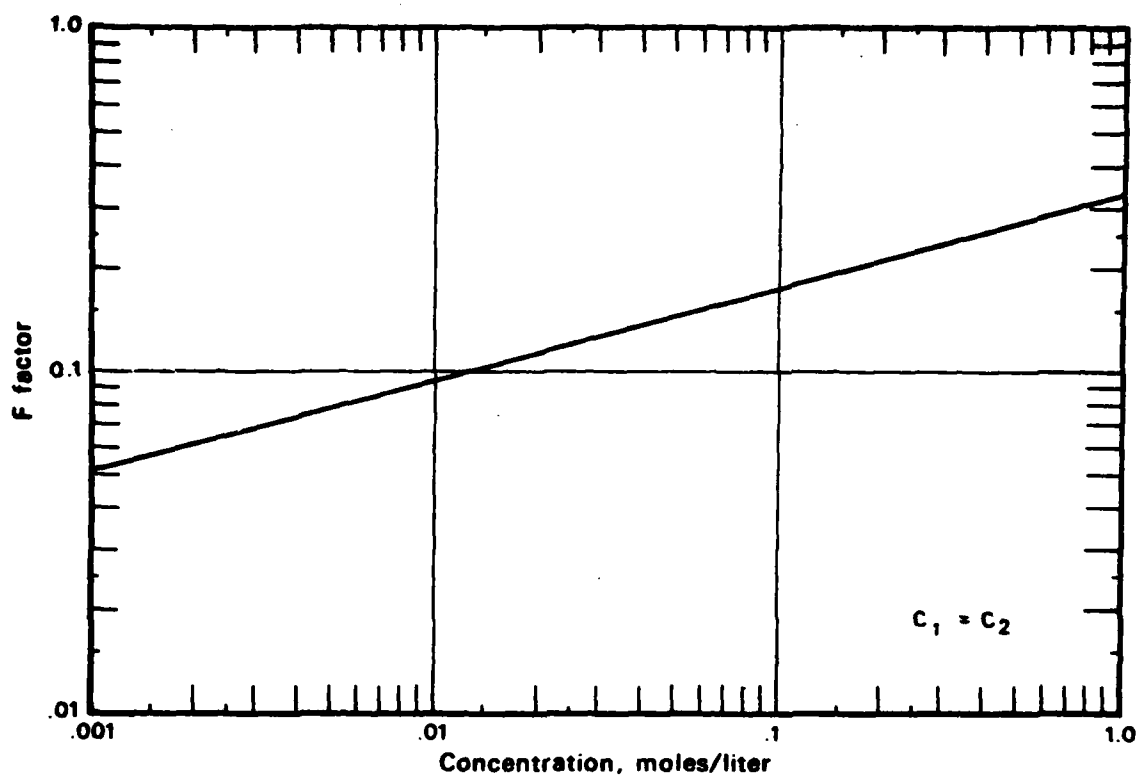


Fig. 2. Plot of F value for equal concentrations of MgSO_4 and NaCl .

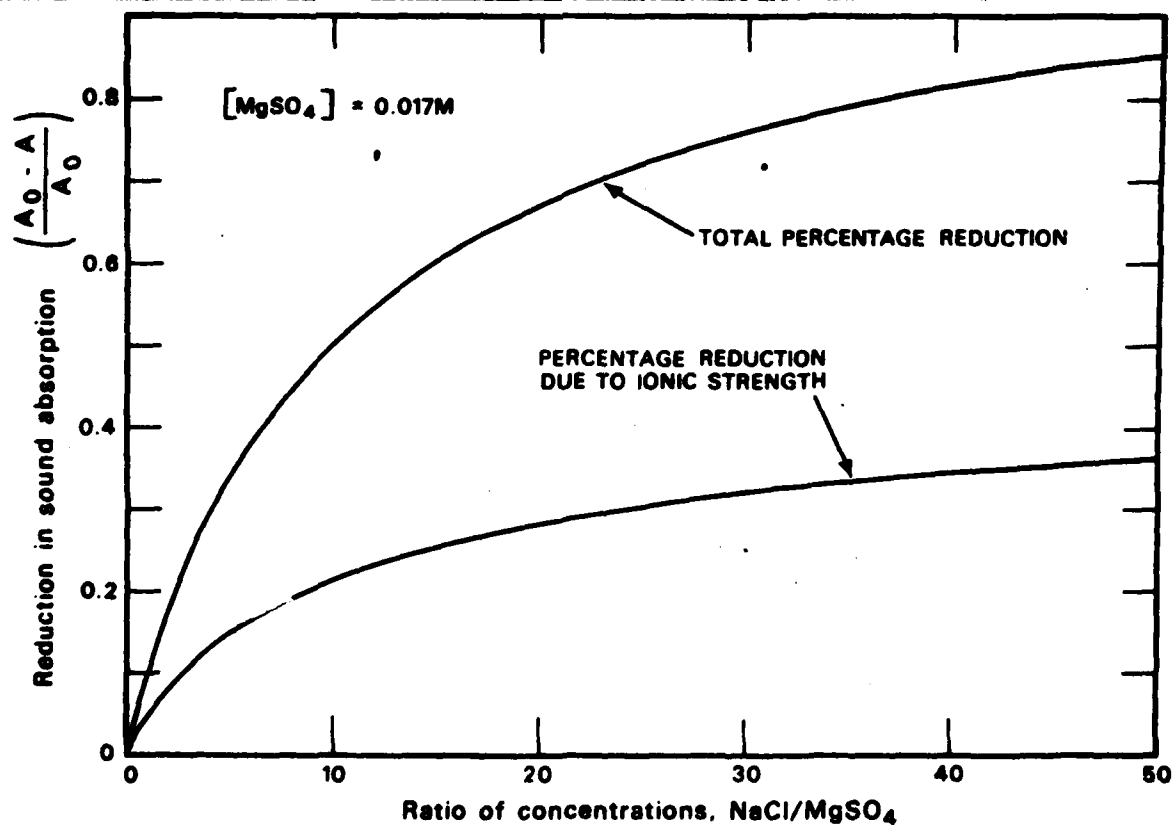


Fig. 3. Comparison of reduction in sound absorption due to ionic strength effects with total absorption for a 0.017 M MgSO_4 solutions as NaCl is added.

TABLE I

Sound Absorption Reduction ΔA at 25° in Mixtures of MgSO_4 and NaCl Aqueous Solutions and Ion-Pair Concentrations as a Function of MgSO_4 Concentration and Various $[\text{NaCl}]/[\text{MgSO}_4]$ Ratios, R

$[\text{MgSO}_4]_0$ moles/l	R	(a)	(b)	(c)	(d)	ΔA %	(e) %	(f) %
			$\times 10^4$ moles/l					
0.001	1	.85	.81	.07	.04	4.9	3.9	1.0
	5		.69	.34	.20	18.3	14.5	3.9
	10		.60	.63	.38	29.0	22.5	6.5
0.005	1	11.04	10.98	1.14	.67	7.6	4.8	2.8
	4		8.47	4.56	2.79	23.3	14.4	9.0
	10		6.50	9.55	6.12	41.1	24.7	16.4
0.01	1	30.12	27.42	4.10	2.47	9.0	4.8	4.1
	5		20.77	16.75	10.76	31.1	16.1	15.0
	10		16.18	28.06	18.97	46.3	23.4	22.9
0.02	1	77.82	69.72	10.48	6.40	10.4	4.6	5.8
	5		50.42	48.44	32.83	35.2	14.6	20.6
	10		37.54	77.70	56.24	51.8	20.8	30.9

(a) = $[\text{MgSO}_4]_0$, MgSO_4 ion-pair concentration in pure MgSO_4 solution.

(b) = $[\text{MgSO}_4]_M$, MgSO_4 ion-pair concentration in mixture.

(c) = $[\text{NaSO}_4]_M$, NaSO_4 ion-pair concentration in mixture.

(d) = $[\text{MgCl}^+]_M$, MgCl^+ ion-pair concentration in mixture.

(e) = Reduction in absorption due to ionic strength.

(f) = Reduction in absorption due to ion-pairing.

TABLE II

Comparison of Experimental and Theoretically Derived F Values for 0.02 M MgSO_4 Mixtures with NaCl Added. The F values are those Calculated According to the Empirical Kurtze and Tamm equation.

Dissociation Constants			F	Remarks
k_{MgSO_4}	$K_{\text{NaSO}_4^-}$	K_{MgCl^+}		
			.21	Kurtze and Tamm
			.129	Hsu
.0062	.1	.178	.134	Predicted in this work
.0062	.2	.356	.093	Doubled dissociation constants of NaSO_4^- and MgCl^+
.0062	100	100	.052	No NaSO_4^- and MgCl^+
.0062	100	.178	.081	No NaSO_4^-
.0062	.1	100	.102	No MgCl^+

TABLE III
Comparison of Stoichiometric Activity Coefficients $\gamma_{\pm} = \alpha f_{\pm}$
in This Paper with Measured Values

m.	This Paper	Robinson & Jones V.P.	Litzke & Stoughton F.P.	
.05	.251	----	----	----
.10	.192	.195	.195	.196
.20	.144	.140	.142	.141
.30	.122	.114	----	.115
.40	.107	.0988	----	.100
.50	.0972	.0882	.091	.089
.6896	----	----	.081	----
.70	.0836	.0747	----	.075
.80	.0788	----	----	.071
1.0	.0712	.0635	.067	.064

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